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Advancing the Predictive Understanding of Low-Temperature Plasmas

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1 Introduction

The purpose of this paper is to characterize the need for improved predictive capabilities in low-temperature plasma (LTP) science, and to identify possible means of accomplishing this. While these means may constitute an initiative of their own, we consider these ideas to have widespread importance to discovery plasma science. Therefore, it is our hope that these ideas are more generally incorporated in future work.

1.1 Definitions

By predictive understanding, we mean the ability to predict some quantity of interest in a given system to sufficient accuracy without the need for calibration of model parameters. The quantity of interest and the level of accuracy required are application-dependent. For example, LTPs have been proposed as a means to convert carbon dioxide to carbon monoxide for the production of synthetic gas [1]. In this case, a quantity of interest might be the conversion efficiency of CO_2 to CO. Meanwhile, the accuracy requirements may derive from the level of confidence required to pursue commercialization.

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1.2 Motivation

There are two primary factors which motivate our belief that advancing predictive understanding is important to LTPs. The first is that it is critical to the engineering and design of new technologies. It reduces empirical design iteration, improves outcomes, allows better quantification of operational margins, and provides insight for failure analysis. In many cases, LTPs have been shown to have potentially significant societal benefits while being limited by a lack of predictive understanding. One such case is that of plasma medicine where LTPs have been shown to selectively kill cancerous cells [2]. However, there are fundamental gaps in the understanding of the biochemical pathways, generation of reactive species, and their transport to target areas [3].

The second reason to pursue predictive understanding is that it is an important path to new discoveries. Indeed, one view of scientific progress is that of testing an established model against new measurements, finding it insufficient, and building a new model to account for the observations. In building new models, one often discovers phenomena that were not previously considered. A recent example of this is the transport of multiple ion species through the same presheath. Initial theoretical models that ions would reach their individual Bohm speed in the pre-sheath. However, detailed measurements proved otherwise and later work established the existence of instability-enhanced collisional friction [4], [5].

1.3 Current State

This subject is also an example of the current status of predictive understanding for LTPs. The last century of work has set out fundamental principles (e.g. the Bohm criterion) that work well in very carefully controlled systems. However, these systems and principles are only a starting point for understanding those of relevance to emerging applications. It should also be pointed out that even for carefully controlled systems, we are frequently lacking in predictive capabilities. For example, recent attempts at benchmarking particle-in-cell codes found large variations in the predicted current density of a simple glow discharge system based on uncertainty in secondary emission coefficients [6]. In another case, a model of a helium-oxygen plasma exhibited significant variations in its predictions when accounting for uncertainty in the best available data [7]. For more complex and/or less controlled systems, our predictive capabilities are even more lacking.

2 Challenges

It is one thing to state that there is a dearth of predictive understanding, but it is an entirely different challenge to identify how to address that problem. In part this is because the need for improvements is directly influenced by a specific system or application. Here, we will focus our concerns on LTP systems at near-atmospheric pressures featuring significant surface interactions. These properties characterize many of the LTP systems envisioned for high-impact applications such as cancer treatment, elimination of antibiotic-resistant bacteria, and destruction of pollutants [8]. While these properties influence our recommendations, we also acknowledge that there are significant needs in the classical LTP systems at significantly reduced pressures and with less complex surfaces.

2.1 Uncertainty

Perhaps the greatest barrier to advancing the predictive understand of LTP systems is the avoidance of uncertainty in comparisons between measurements and models. Without an accounting for uncertainty in both model and measurement, it is impossible to judge agreement, and thus impossible to judge model sufficiency. If we wish to refine our models and understanding of LTP systems, we must work to better understand and quantify uncertainty.

A large source of uncertainty in LTP models originates in the uncertainty of a model's input parameters. This can include uncertainty in fundamental data, such as that described by Turner [7]. However, it can also originate in uncertainty about the actual experiment's properties, as in [6]. In either case, this uncertainty leaves modelers with significant leeway to "calibrate" results by choosing values that give the appearance of agreement with experiment. In the best case, such a model may be predictive for a single system in a narrow range of operation. However, this ultimately gives a false impression of a broad predictive capability where none exists.

Measurements are also subject to a large degree of uncertainty with a similarly large number of origins. One such source is the challenge in reproducibility. LTP systems are often unique designs that are not specified in sufficient detail. This is an old problem that has been previously solved through the use of reference systems [9]. A more challenging source of uncertainty is the heavy model-dependence of most LTP diagnostics. Sheath theory, collisional-radiative models, line-shape analysis, and many other models are often required to infer physical quantities from electrical or optical signals.

Unfortunately, there is no simple or universal solution to the issue of addressing uncertainty in LTP systems. Instead, the LTP community must incorporate these principles in comparisons between model and measurement. In some instances, new ways to quantitatively assess uncertainty may be required, such as in the case of stochastic models. Even where this is not the case, a true accounting for both model and measurement uncertainty is likely to be challenging and time-consuming. However, it is a necessary component to advancing our predictive understanding of LTPs.

2.2 Chemistry

A characteristic challenge of almost all the envisioned systems is a degree of chemical complexity which ranges from merely large to extreme. This is a particular feature of plasma medicine, water remediation, combustion, catalysis, and many others. While historical systems emphasized the use of noble gases, these applications frequently feature many different molecular systems and plasma-generated byproducts. The resulting reaction networks are extensive and made even more challenging by the non-equilibrium characteristic of LTPs. A "simplified" reaction set for atmospheric pressure plasma jets contains 84 species and 1880 reactions [10].

To address this challenge, we must expand the set of diagnostics available to assess the densities and distributions of relevant species as well as their accuracy. In this case, the LTP community could learn from the combustion community where techniques to assess the plethora of neutral species, such as advanced mass spectometry and (TA)LIF, have been fruitful. However, not only must the LTP community adopt techniques used elsewhere, it must surpass them. The non-equilibrium nature of LTPs implies a greater variety of species of interest and the loss of many simplifying assumptions. For example, vibrational non-equilibrium in LTPs dramatically changes the attachment and recombination lifetimes in air plasmas and predictive models at long timescales must accurately account for this effect.

We must also address the substantial requirements for fundamental physical data. This includes reaction rates, but also integral and differential cross sections when kinetic effects are important. Associated with this is the need to limit or reduce the complexity of reaction networks as much as possible, while still maintaining predictive capabilities. In equilibrium systems, this has accomplished using formal methods such as principal component analysis. While this technique has seen use in plasma systems [11], there is still a clear need to address the dynamic and non-equilibrium nature of LTP systems.

2.3 Collisions

High collision frequencies amongst neutral and charged particles also presents a new and unique problem for LTP systems. While low pressure LTP systems are strongly dominated by the electromagnetic fields, near-atmospheric pressure sources are often in a regime where collision frequencies are comparable to the electron plasma frequency. This has repercussions in the transport of particles, equilibrium, and diagnosis of such plasmas.

A fundamental assumption in many plasma models is that particle collisions are binary encounters. This appears in the collision models employed for numerical simulations and the collision operators employed in the Boltzmann equation. However, multi-body effects are increasingly important at higher densities, particularly with attempts to generate plasmas in liquids and solids. Similar conditions can also give rise to strongly-coupled systems where large-angle scattering events can dominate. To address this, models for future LTP systems will require new theory to address multi-body interactions and numerical models to successfully describe strongly-coupled plasmas.

Collisions also challenge traditional plasma diagnostic methods. Electrical probe analysis employing theories of collisionless sheaths are no longer valid in these new regimes. Meanwhile, optical diagnostics can face challenges due to quenching of excited states, radiation trapping, and more. In some cases, old diagnostic tools may be revised to address highly collisional systems. The use of advanced models and simulations may be used to improve signal analysis. Alternatively, the incorporation of new technology, such as femtosecond lasers in laser collision-induced fluorescence [12], may be a path forward. However, some LTP systems will likely require fundamentally new means to assess their properties.

2.4 Surfaces

Even the earliest studies of LTPs observed that the boundary between a plasma and a surface was of significant interest. The importance of boundaries is evident in how they control whether or not a system breaks down, as in Paschen's law, or the manner in which they can determine the plasma potential of a system. Yet the understanding of them is essentially limited to ideal cases (e.g. a pure noble gas between ideal conductors) and reproducibility is very challenging from a surface perspective. For example, [13] reports on the wide variety of secondary emissions coefficients that are possible for nominally identical materials.

At the most basic level, better measurements of surface properties for carefully controlled systems would be a boon to predictive capabilities. In particular, the literature is bereft of data at low energies for real surfaces, as opposed to ideal ones (atomically pure, monocrystalline, ...). However, this is not enough. Surfaces are subject to change due to chemi-sorption, cathode spots, local fields, and many other phenomena. This implies a need to not only understand fundamental surface *ex situe*, but to develop the capability for *in situ* surface measurements where a plasma is present.

Unfortunately, it is unrealistic to conduct the exhaustive process of measuring every possible surface in every combination of conditions. Instead, advanced material models need to be developed to provide a more clear understanding of the behavior of real surfaces. As with the understanding of reaction networks, the LTP community can draw expertise from other areas such as surface science. However, the requirements of LTP systems will eventually require not just incorporating the existing body of knowledge, but advancing it. Only by incorporating novel surface models into future plasma simulations will there be a chance to produce reliable predictions.

3 Conclusions

In this paper, we have argued that prospective LTP applications and discovery plasma science would greatly benefit from advancing predictive capabilities in LTPs. Such an advancement requires progress on many fronts. From a technical perspective, there are significant gaps in our ability to model and measure systems with complex chemistry, high collisionality, and realistic surfaces. Each of these areas will require significant modeling and experimental efforts in order to support new technological advances.

However, there are not just physical challenges for the LTP community, but methodological ones too. The prevailing approach to comparing models and experiments downplays the importance of uncertainty. The result is an emphasis on qualitative comparisons that prioritize trends over absolute values, and an inability to judge model sufficiency. A more serious effort to understand and quantify uncertainty in LTPs is required in order to advance our predictive understanding of LTPs.

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